RESULTS OF CURRENT STUDIES ON COATED TANTALUM ALLOY SHEET AT NASA LANGLEY RESEARCH CENTER

By Bland A. Stein and Gregory R. Wichorek

NASA Langley Research Center
Langley Station, Hampton, Va.

Presented at the Thirteenth Meeting of the
Refractory Composites Working Group

[redacted]

Seattle, Washington
July 17-20, 1967

RESULTS OF CURRENT STUDIES ON COATED TANTALUM ALLOY SHEET AT NASA LANGLEY RESEARCH CENTER

By Bland A. Stein and Gregory R. Wichorek

NASA Langley Research Center

INTRODUCTION

Recent NASA considerations of the feasibility of hypersonic cruise vehicles have indicated that leading-edge regions of such aircraft may operate at temperatures from 2000° to 3000° F for times up to 1 hour during each flight (refs. 1 and 2). Coated tantalum alloys are candidate materials for this application. Coatings which were found unsuitable because of poor low pressure behavior in previously considered applications, such as in entry vehicle structures, must be reconsidered for this application since ambient pressures are considerably higher. Such a coating is the slurry-dip aluminum-tin-molybdenum coating which has been commercially available for several years. Results of oxidation and mechanical property tests on thin Ta-10W alloy sheet protected with this coating are presented herein.

Another problem area for a hypersonic cruise vehicle is the nose cap region where temperatures in excess of 3000° F are expected. Current refractory metal coating technology at such temperatures is not well advanced. The problem of spalling caused by thermal expansion mismatch between an oxide coating and a refractory metal substrate is a major detriment to the use of coated refractory metals in this application. A concept for a coating system for this area is described: a gradated intermetallic/oxide coating. This type of coating, applied by electrophoretic deposition, was investigated as a means of eliminating the spalling problem. Results of oxidation tests on thin tantalum alloy sheet

L-5764

with two coatings of this type, presented herein, indicate this concept to be a promising solution of the spalling problem. However, other parameters of the coating process, such as better sintering of the oxide, need further development before long coating lifetimes can be attained.

SPECIMENS AND COATINGS

The specimens used in this study were small oxidation coupons, tensile strips, and leading-edge segments. Specimen configurations and dimensions are shown in figure 1. These specimens were fabricated from vacuum annealed tantalum-10 percent tungsten (nominal by weight) alloy sheet, 0.008- and 0.025 inch thick (nominal).

A slurry-dip 23.5 percent (by weight) aluminum-71 percent tin-5.5 percent molybdenum coating was applied to the oxidation coupons, tensile strips, and leading-edge specimens by the Sylvania Corporation in cooperation with the U.S. Air Force. Details of this coating process are given in reference 3. A few specimens were coated with a modification of this coating containing 23.5 percent aluminum-69.5 percent tin-7 percent molybdenum (ref. 4).

The gradated coatings were applied by Vitro Corporation to oxidation coupons and leading-edge specimens by electrophoretic codeposition of oxide and intermetallic powders, followed by isostatic cold pressing and sintering at temperatures above 3000° F in argon. Details of the coating process, developed by Vitro Corporation, are presented in reference 5. Specimens of two of these gradated coatings were studied: Coating 1 containing calcia stabilized zirconia as the oxide and molybdenum disilicide as the intermetallic and coating 2 containing calcia stabilized zirconia with titania added as the oxide and tungsten disilicide as the intermetallic.

TEST PROCEDURES

Oxidation Tests

Static oxidation tests were conducted in vertical tube furnaces. The tantalum-alloy coupons were supported in high-purity alumina boats. During the cyclic tests the boats were rapidly inserted into the furnaces, exposed at temperature for 1 hour or 6 minutes, then were rapidly removed from the furnace and cooled to room temperature. The coupons reached 95 percent of test temperature within 30 seconds. The specimens were weighed after each cycle; visual evidence of tantalum oxide constituted coating failure. Tests were run at sea-level atmospheric pressure. Test temperatures ranged from 2000° to 2900° F. Tests were discontinued at 50 hours if no failures had occurred.

Dynamic oxidation tests were conducted on leading-edge segments in an arc-heated subsonic air jet with a 4-inch-diameter exit exhausting to sea-level atmospheric pressure. This produced a subsonic airstream with a mass flow of 0.4 pound of air per second. The specimens were attached to a water-cooled sting and subjected to the vertical airstream as shown in figure 2. In each cyclic test the specimen was rapidly inserted into the hot airstream, held for 6 minutes, then rapidly removed from the airstream and cooled to room temperature for visual examination. Tests were discontinued when coating failure was observed (visual evidence of tantalum oxide) or when an accumulated exposure time of 2 hours (20 cycles) was achieved. Test temperatures ranged from 2000° to 3000° F. Temperatures were measured using an optical pyrometer at a wavelength of 0.65 micron with corrections for assumed coating spectral emittances of 0.7 for the aluminum-tin-molybdenum coating and 0.8 for the gradated coatings.

Tensile Tests

Room-temperature tensile tests were performed at sea-level atmospheric pressure in a hydraulic testing machine at nominal strain rates of 0.005 per minute to yield and 0.050 per minute to failure. Strains were monitored through yield with optical strain gages which were read while the strain rate was maintained. Tensile elongations were measured over a 1-inch gage length.

Elevated-temperature tensile tests were performed in a screw-powered testing machine. Specimens were resistance heated to test temperature as monitored by an optical pyrometer (corrected for the assumed emittance noted previously); the specimens were held at temperature for 6 minutes before loading to failure at the strain rates noted in the preceding paragraph. Test temperatures ranged from 1700° to 2900° F.

RESULTS AND DISCUSSION

Aluminum-Tin-Molybdenum Coating

<u>Oxidation tests</u>.- Results of oxidation tests on Al-Sn-Mo coated Ta-10W alloy are shown in figure 3. The graph at the left shows the results of static tests on coupons for two cyclic exposure conditions. In the 1-hour cycles lifetimes ranged from about 50 hours at 2000° F to about 5 hours at 2900° F. The 6-minute cycles reduced coating life considerably, as compared to the 1-hour cycles.

The graph at the right in figure 3 indicates the effect of flowing air on the life of coated-tantalum-alloy specimens for 6-minute cycle exposures. The static air curve is reproduced from the graph at the left for comparison. The conditions in the arc-jet tests lowered coating lifetimes obtained under static conditions considerably at temperatures above 2400° F for the aluminide coating containing 5.5-percent molybdenum. A modified aluminide coating containing

7 percent molybdenum has been developed. As shown in figure 3, this coating has exhibited longer lifetimes in a few flowing air tests. A possible explanation of this increased effectiveness with higher molybdenum content in the coating is based on an increase in viscosity of the liquid layer which forms in this coating during high-temperature exposures. This is discussed in more detail in reference 6.

In summary of the oxidation test results, lifetimes of 1 hour or more were achieved by the aluminum-tin-5.5-percent molybdenum coating in cyclic tests conducted in static air at temperatures up to 2900° F, but in flowing air cyclic tests, lifetimes below 1 hour were noted at 2700° and 3000° F. Based on several flowing air tests, addition of more molybdenum to the coating appeared to provide longer lifetimes from 2400° to 3000° F in the airstream.

Tensile tests.- The utilization of coated tantalum alloys is not only dependent on the oxidation protection provided by the coating, but also on the mechanical properties of the substrate after coating application and subsequent service.

In figure 4 the results of room-temperature tensile tests are shown for as-received uncoated and coated tantalum-alloy specimens fabricated from 0.008-inch and 0.025-inch sheet. The 5.5- and 7.0-percent molybdenum coatings had little effect on the ultimate stress and yield stress of the tantalum-alloy substrate, but they did increase the elastic modulus of the 0.008-inch sheet on the basis of the original specimen thickness before coating. This apparent increase in stiffness was probably due to the formation of an aluminide layer next to the substrate. The two coating processes had the greatest effect on the elongation; the coatings reduced the elongations of the 0.008-inch and 0.025-inch sheet by 50 and 30 percent, respectively.

Figure 5 shows the effect of elevated temperatures on the tensile properties of the coated tantalum alloy. In the temperature range investigated, from 1700° to 2900° F, no unusual or significant behavior is apparent in the ultimate stress, yield stress, and elastic modulus of the coated tantalum alloy. A large variation in substrate thickness resulted in slight variations in these properties. Elongations were different for the two thicknesses, however. Most critical is the elongation of only 2 percent at 1700° F for the 0.008-inch sheet.

Finally, figure 6 shows the effect of time at elevated temperature on the tensile properties of the 0.008-inch tantalum-alloy sheet coated with the 5.5-percent molybdenum coating. Specimens were exposed to 2600° F and tested both at room temperature and at 2600° F. The ultimate stress and yield stress of the coated tantalum alloy at both test temperatures were not significantly affected by the exposure time at 2600° F. During the first hour exposure, the decrease in elastic modulus at room temperature and the increase in modulus at 2600° F is possibly due to reactions between the coating and substrate in addition to those which occurred during the coating process. Again reduction in elongation is significant. Most critical is the room-temperature elongation of 1 percent after exposure to 2600° F for 5 hours.

In summary of the tensile test results, the tantalum-alloy sheet coated with the aluminide coatings retained adequate strength and stiffness for leading-edge applications to 2900° F although the elongation in some cases was significantly reduced.

Gradated Coatings

Concept.- The concept of the gradated coating is indicated by the sketch at the top of figure 7. The coating should consist of a dense oxide at the outer surface for good oxidation protection and an intermetallic compound at the

coating-substrate interface for best coating-substrate compatibility. The oxide and intermetallic are continuously gradated through the coating to alleviate the thermal expansion mismatch between oxide and metal which has caused spalling of previous oxide coatings. One of the best methods of application of such a coating is electrophoretic codeposition of oxide and intermetallic powders.

Photomicrographs of the two coatings investigated are shown in the lower part of figure 7. In coating 1 the oxide is calcia stabilized zirconia and the intermetallic is molybdenum disilicide. In coating 2 the oxide is calcia stabilized zirconia with 2 percent titania added and the intermetallic is tungsten disilicide. These complex coatings are approximately 5 mils in thickness. A serious problem with these coatings has not yet been solved; sintering of the oxide-rich portion of the coatings has not yielded sufficiently dense outer layers to prevent penetration of the coating by atmospheric gases. The porosity in the coatings is evident, as shown by the black areas in figure 7. In an attempt to improve oxidation resistance in these coatings, a siliconizing treatment was applied by pack cementation. One significant difference between the two coatings is the small gradated zone in coating 1 as compared to coating 2; even in coating 2 the gradation zone is relatively thin compared to the coating thickness. However, it will be shown that even a thin gradated layer can eliminate or reduce spalling.

Oxidation tests.- Photographs of tested specimens of coatings 1 and 2 on 8-mil-thick Ta-10W alloy sheet are shown in figure 8. Coupon specimens were subjected to 6-minute cycle static air tests at 2600° F in a tube furnace. Considerable spalling of the oxide layer was evident for coating 1 after the tests. No spalling was noted for coating 2 but a small coating failure is apparent and tantalum oxide is in evidence at the failure site. The leading-edge

specimens were subjected to 6-minute cycle tests in flowing air at 2700° F in an arc jet. Again, spalling of the oxide layer was noted for coating 1 but no spalling was evidenced in coating 2 after the tests. This was probably due to the better gradation in coating 2 as compared to coating 1.

However, the most severe problem with the coatings was the porosity, previously noted. This resulted in poor oxidation behavior as shown in figure 9. Time to failure is shown for coatings 1 and 2 subjected to cyclic oxidation under static and flowing air conditions. For comparison, time to failure is indicated for other existing aluminide and silicide coatings exposed to 1.0-hour cyclic oxidation (ref. 2). The short oxidation lives of gradated coatings 1 and 2 can be attributed to porosity and poor self-healing characteristics. The data for the Al-Sn-Mo coatings discussed earlier fall in the shaded region of figure 9.

CONCLUDING REMARKS

Current results of an investigation of oxidation resistant coatings for Ta-10W alloy sheet indicate that:

1. The aluminum-tin-5.5-percent molybdenum coating provided protection for at least 1 hour in static air tests up to 2900° F, but considerably lower lifetimes were achieved in flowing air tests. Addition of more molybdenum to the coating appeared to increase lifetimes in flowing air tests. Under static test conditions, coating lives in 6-minute cycle tests were considerably shorter than those for 1-hour cycle tests.

2. The tantalum alloy with the aluminum-tin-molybdenum coatings retained adequate strength and stiffness for leading-edge applications at temperatures to 2900° F but low elongation at 1700° F was noted. Elongation of 8-mil sheet

at room temperature was significantly decreased by the coating process. Subsequent exposures at elevated temperature resulted in further reductions in elongation.

3. Gradation has been shown to improve resistance to spalling in intermetallic/oxide coatings subjected to cyclic exposures to elevated temperature. Short coating lifetimes obtained with the two gradated coatings investigated indicate that further developments are required to reduce porosity in these coatings.

REFERENCES

1. Heldenfels, R. R.: Structural Prospects for Hypersonic Air Vehicles. Presented at the 5th Congress of the International Council of the Aeronautical Sciences. ICAS Paper No. 66-31, London, England, September 1966.
2. Stein, Bland A.; Illg, Walter; and Buckley, John D.: Structural Materials for Hypersonic Aircraft. Proceedings of Conference on Hypersonic Aircraft Technology, NASA SP-148, May 16-18, 1967, pp. 485-499.
3. Sama, Larry: High Temperature Oxidation-Resistant Coatings for Tantalum Base Alloys. ASD-TDR-63-160, U.S. Air Force Materials Laboratory, 1963.
4. Reznik, B.; Sama, L; Priceman, S.; and Lawthers, D.: Development of Oxidation Resistant Coatings for Refractory Metals. Summary of the Eleventh Refractory Composites Working Group Meeting. AFML-TR-66-179, U.S. Air Force Materials Laboratory, July 1966, pp. 333-351.
5. Campbell, P. F.; Gebler, K. A.; and Ortner, M. H.: Electrophoretic Deposition of Gradated Oxidation Resistant Coatings on Tantalum-10 Tungsten Alloy. NASA CR 66068, Prepared under contract NAS1-3533 by Vitro Laboratories, New Jersey, 1965.
6. Stein, Bland A.; and Lisagor, W. Barry: Oxidation and Embrittlement in Silicide-Coated Columbium-Alloy and Aluminide-Coated Tantalum-Alloy Sheet. Presented at the Fourth Symposium on Refractory Metals, The Metallurgical Society of AIME, French Lick, Indiana, October 1965.

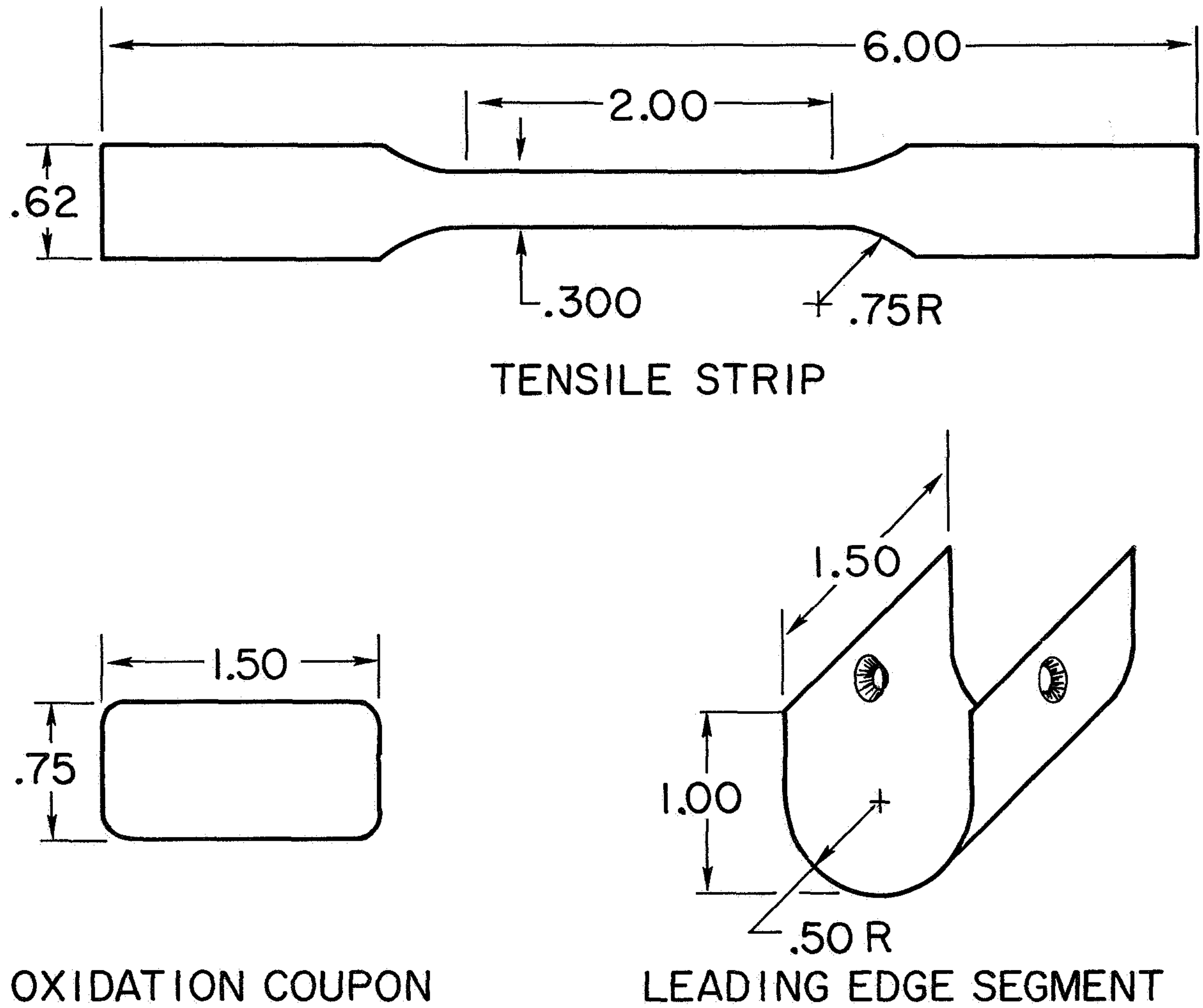

Figure 1.- Specimen configurations. Dimensions in inches.

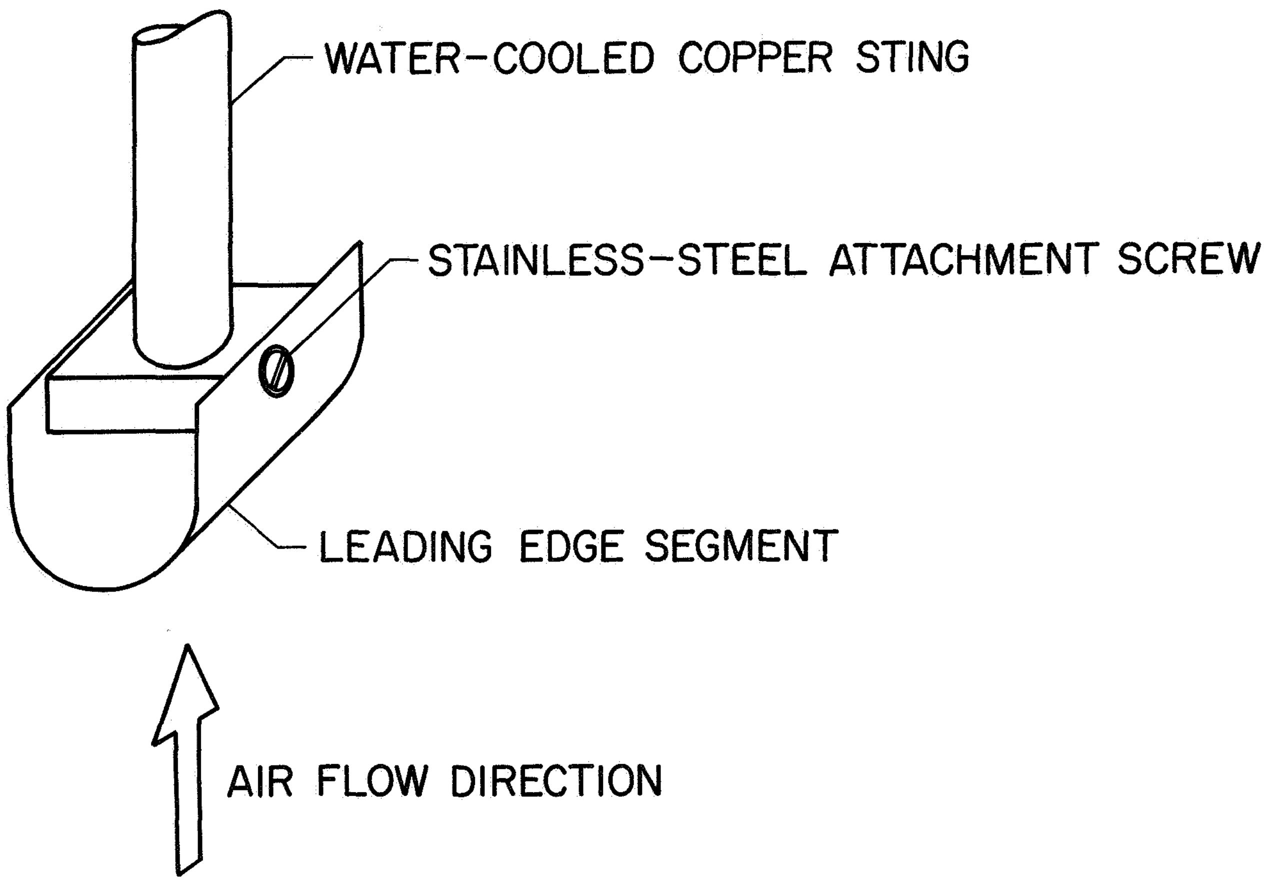

Figure 2.- Diagram of leading-edge segment in arc-heated subsonic air jet test.

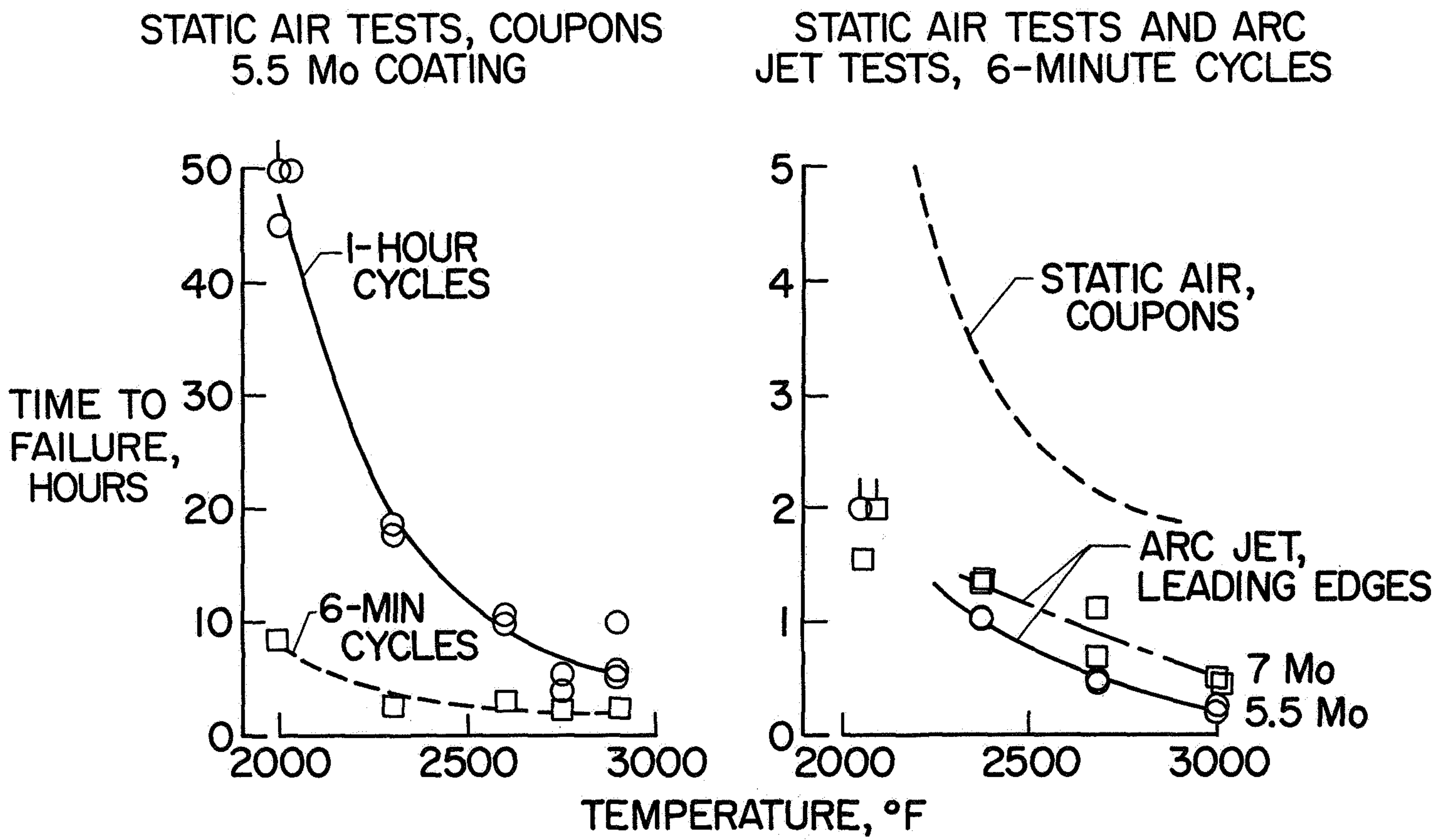

Figure 3.- Oxidation test results for aluminum-tin-molybdenum coated Ta-10W sheet specimens tested in air at sea-level atmospheric pressure.

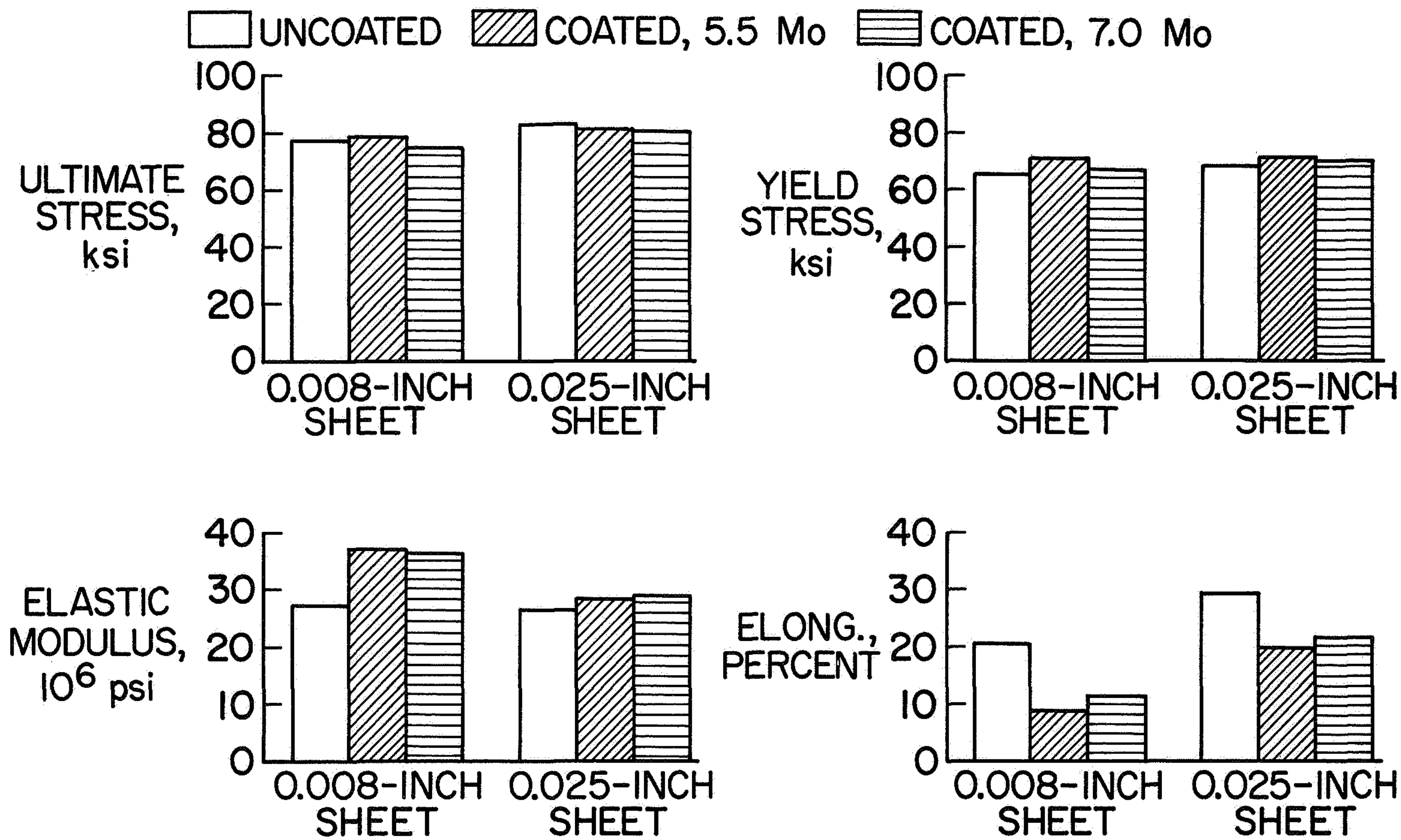

Figure 4.- Room temperature tensile properties of as-received Al-Sn-5.5Mo and Al-Sn-7Mo coated Ta-10W sheet specimens.

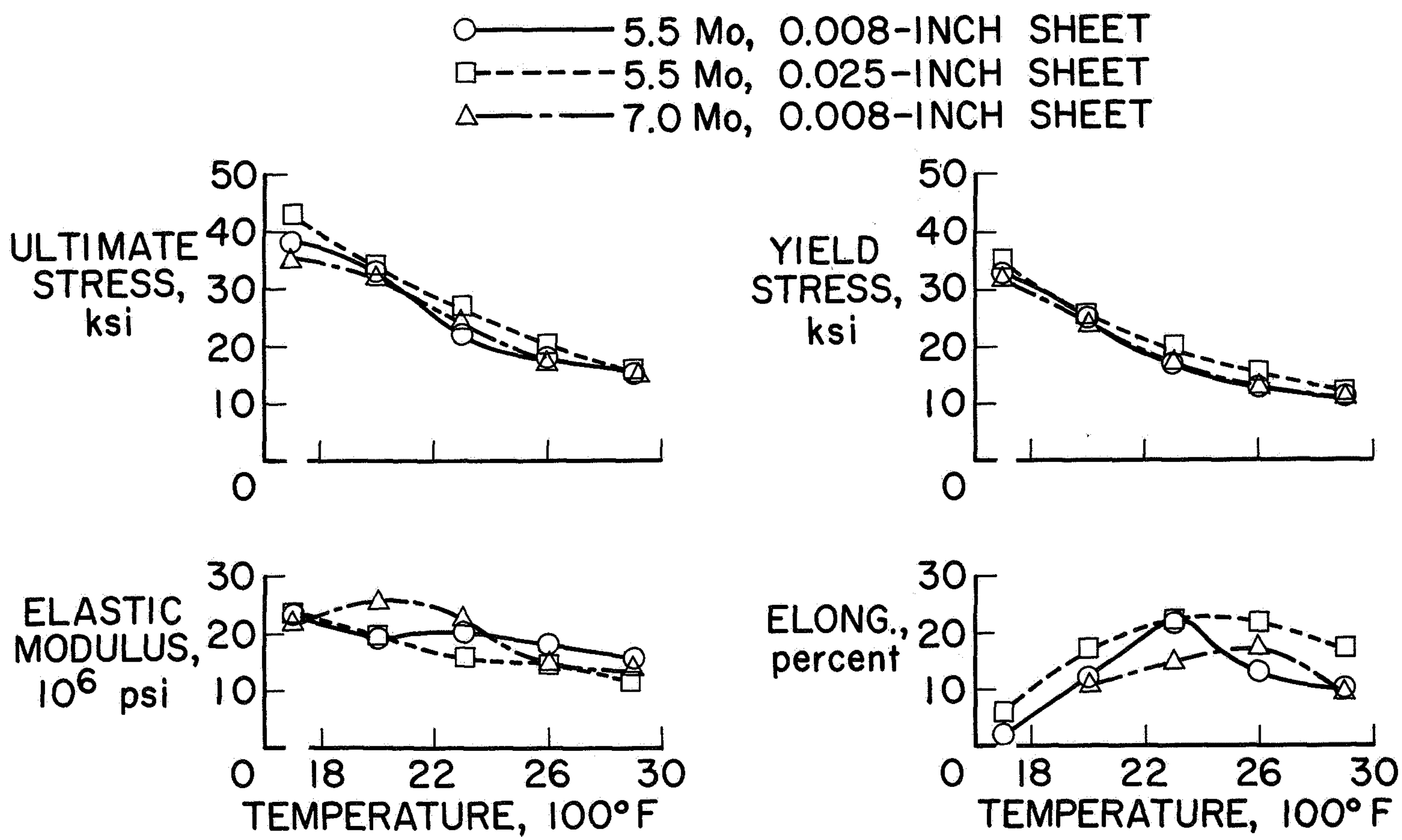

Figure 5.- Elevated temperature tensile properties of Al-Sn-5.5Mo and Al-Sn-7Mo coated Ta-10W sheet specimens.

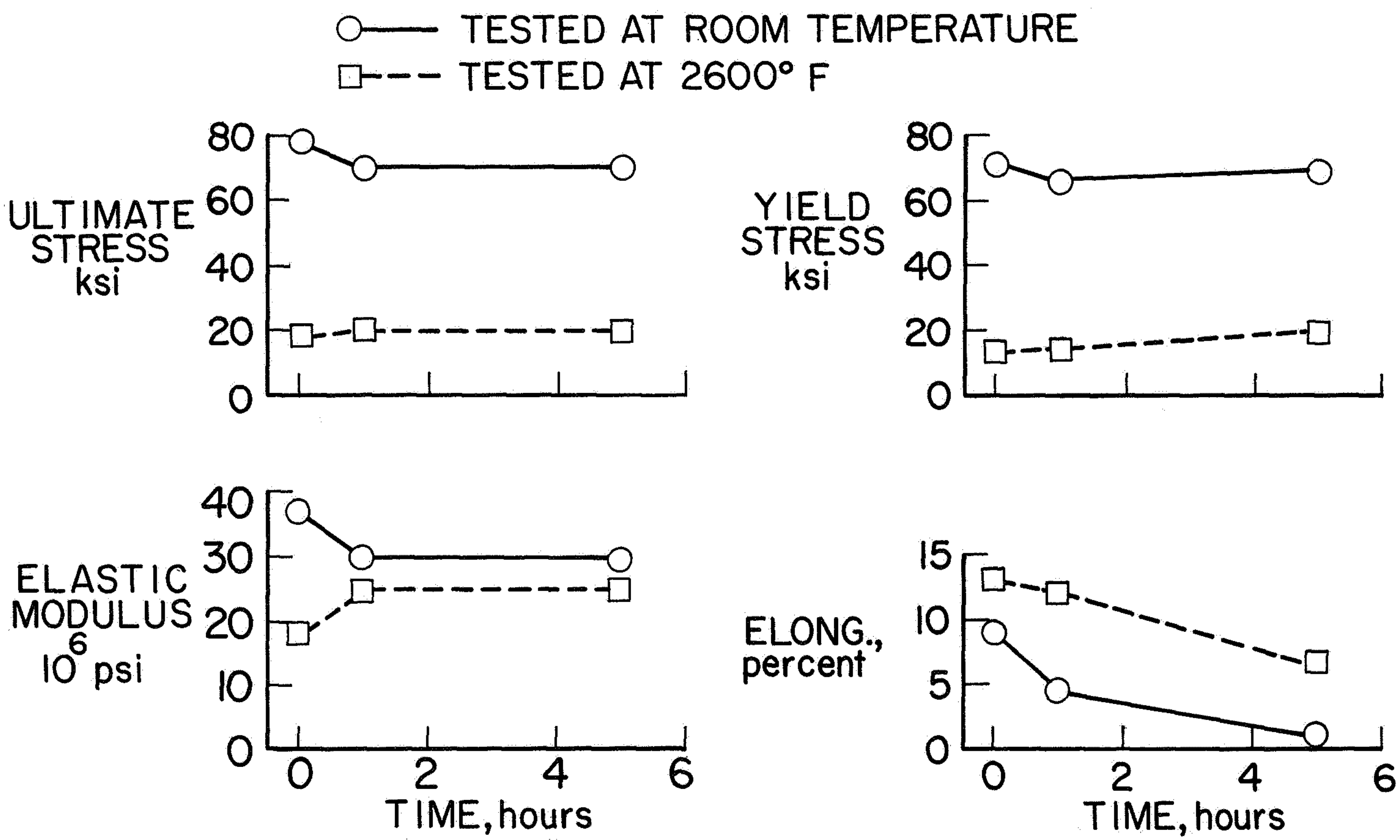

Figure 6.- Effect of 2600° F exposures in air at sea-level atmospheric pressure on room temperature and 2600° F tensile properties of aluminum-tin-5.5-percent molybdenum coated Ta-10W sheet specimens, 8 mils thick.

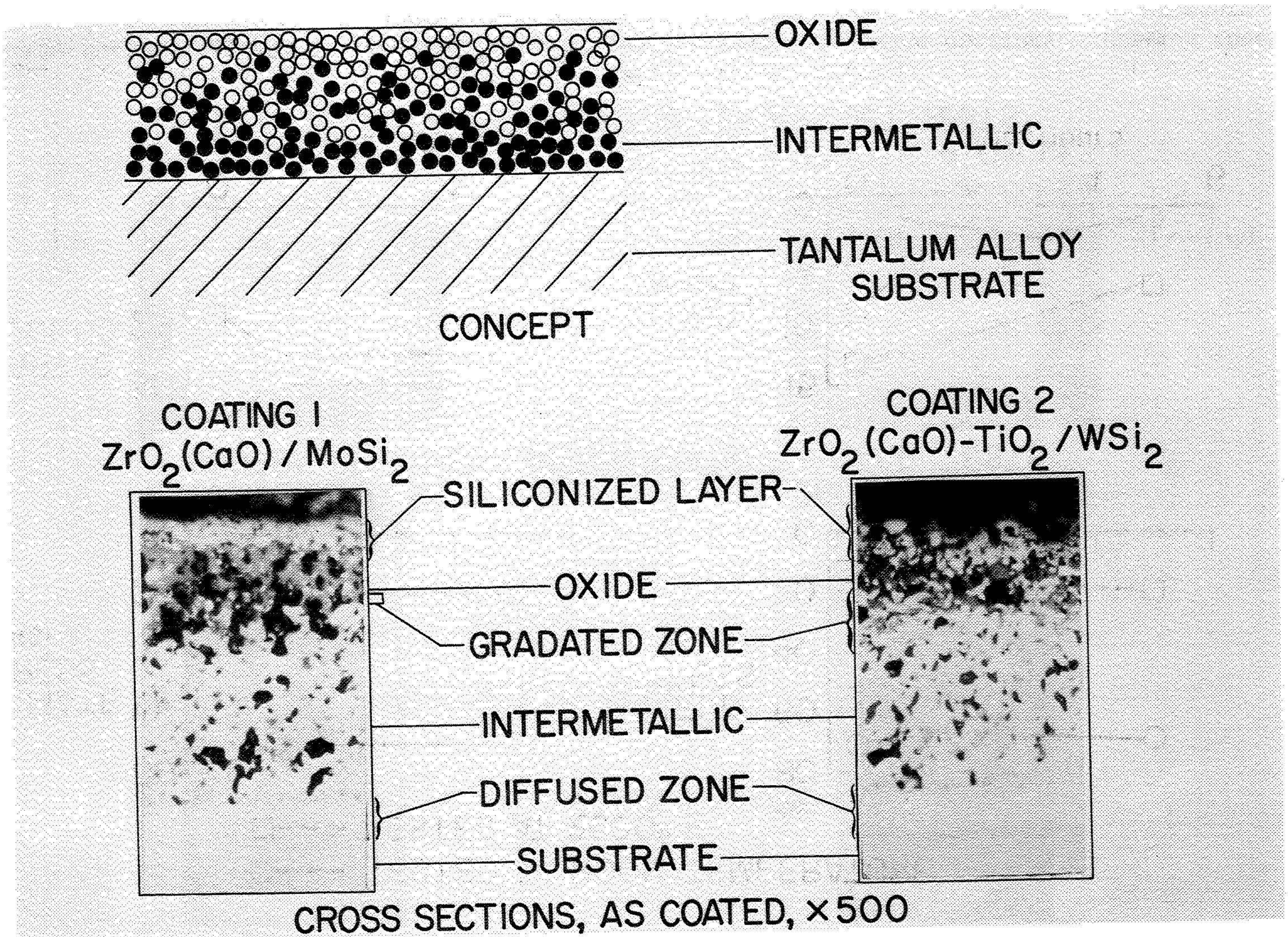

Figure 7.- Concept and as-coated cross sections of gradated intermetallic/oxide coatings on tantalum alloy sheet.

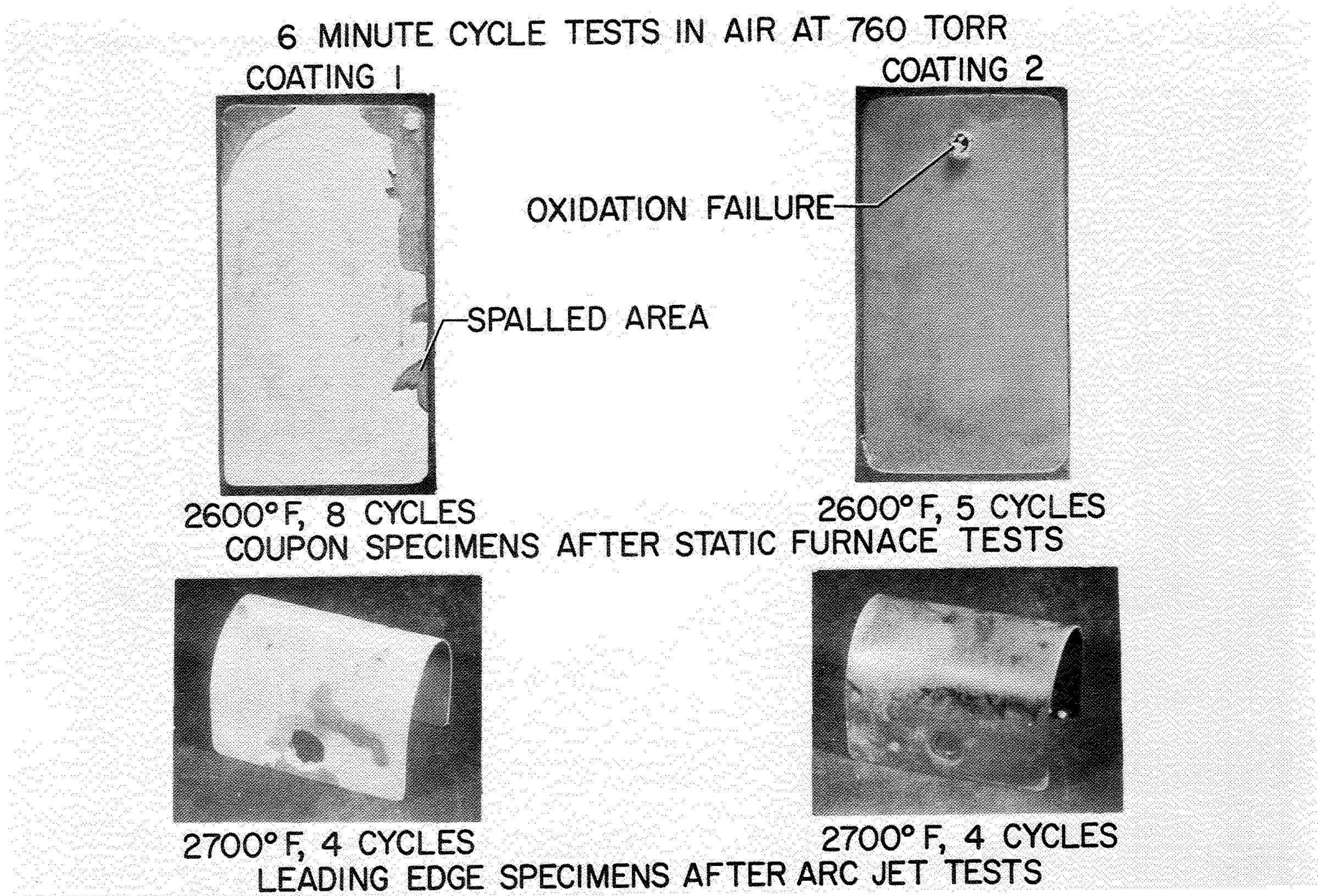

Figure 8.- Photographs of specimens of gradated intermetallic/oxide coatings on Ta-10W sheet specimens after 6-minute cycle oxidation tests in air at sea-level atmospheric pressure.

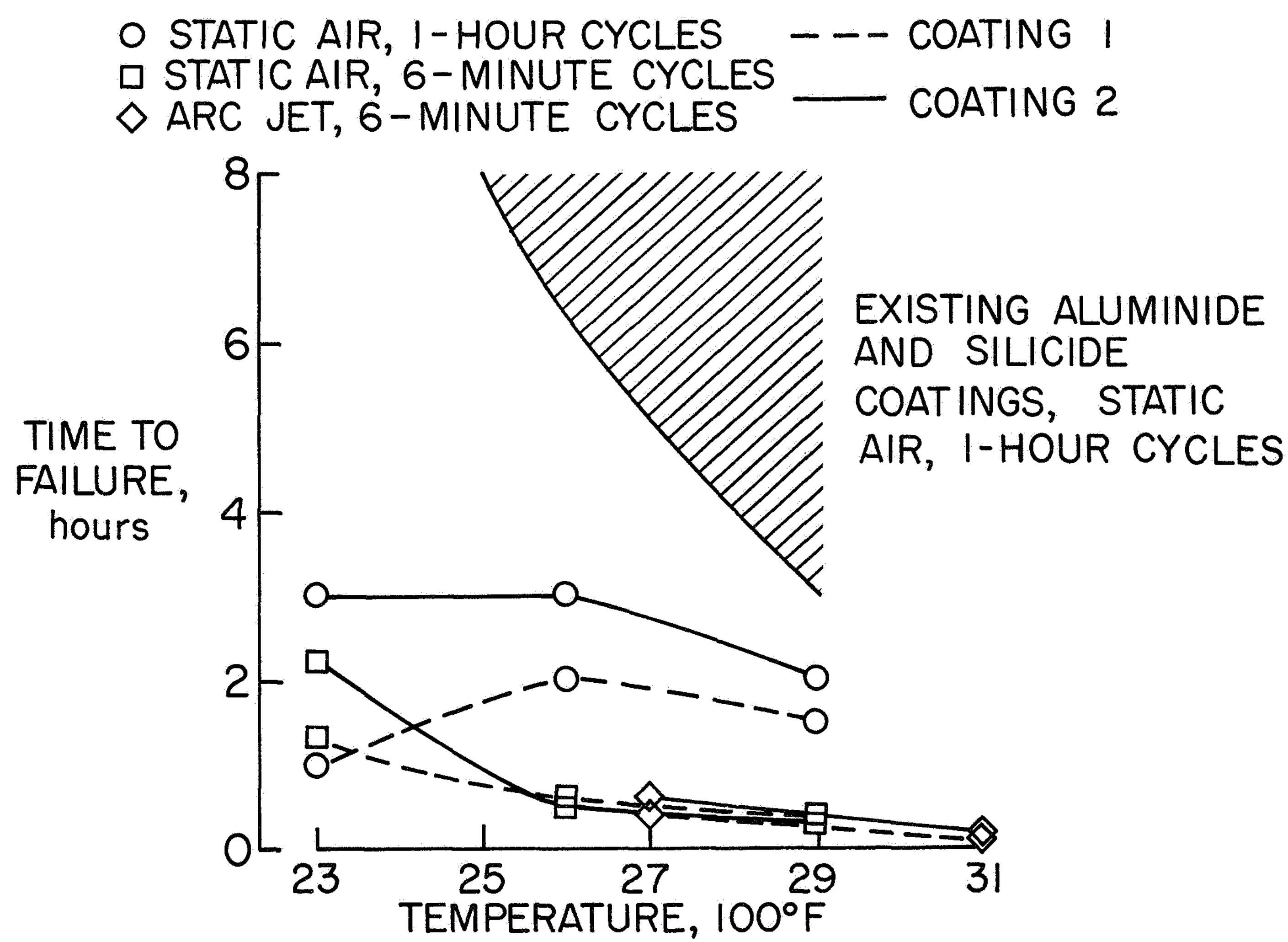

Figure 9.- Oxidation test results for specimens of intermetallic/oxide coatings on Ta-10W alloy sheet tested in air at sea-level atmospheric pressure.

NASA-Langley, 1967